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Chlorination of 3β-hydroxyl-5-Δ steroids with anhydrous ferric chloride

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Abstract

Treatment of 3β-hydroxyl-5-Δ steroids with anhydrous $FeCl_3$ in CH_2Cl_2 afforded reasonable yields of the corresponding alkyl chlorides with a retention of configurations. The structures of the chlorine-exchanging products were determined by NMR and HRMS spectra. The absolute configurations were confirmed by X-ray crystal analysis of 3β-chloro-androst-5-en-17-one. The generality and scope of the reaction were also investigated.

Keywords: Anhydrous $FeCl_3$; Chlorination; Configuration-retention; Homoallylic carbonium ion

1. Introduction

Dehydroepiandrosterone (DHEA, 3β-hydroxyandrost-5-en-17-one) has a number of beneficial biological effects in animals [1] including the inhibition of the enzyme glucose-6-phosphate dehydrogenase (G6PDH) [2]. However, it can be metabolised to estrogen with known tumor-promoting activity [1] via the hydrolysis of steroid sulfates by steroid sulfatases [3]. Thus, there have been a number of reports describing the development of steroid sulfatase inhibitors in recent years [4–6]. The substitution or protection of the 3β-hydroxyl group on the A-ring may prohibit its metabolism into estrogen. Some hydrophobic A-ring steroids are also excellent inhibitors of the G6PDH [7].

Alkyl chlorides are both useful synthetic intermediates and valuable products [8]. Many methodologies for the conversion of alcohols into their corresponding alkyl chlorides have been developed and widely used over the past decades [9–11]. Many methods have certain drawbacks, however, such as the inversion of configurations or the occurrence of extensive racemization when optically active alcohols are used [12]. But some documents [13,14] describe the conversion of steroid compounds into their corresponding chlorides with a full retention of configurations. Recently, we found that anhydrous ferric chloride in dichloromethane could lead to such a conversion of the 3β-hydroxyl-5-Δ steroids. Metal chlorides [15,16] are generally used as Lewis acids to catalyze various reactions, including acylation, and a few reports of their direct utilization as chlorinating reagents have been documented [17,18].

2. Experimental

2.1. General procedures

All solvents were dried by standard procedures. Anhydrous ferric chloride and 3β-hydroxyl-5-Δ steroids are commercially available. The saturated 3-hydroxyl steroids were obtained by hydrogenating their corresponding 3β-hydroxyl-5-Δ steroids in the presence of a Pd/C catalyst. Thin-layer chromatography (TLC) was performed on glass plates precoated with silica gel (5–40 μm) to monitor the reactions and to certify the purity of the reaction products. Visualization was accomplished by spraying chromatograms with 10% ethanolic sulfuric acid and charring them on a hot plate. Column chromatography was carried out on silica gel (200–300 mesh). Elemental analysis was carried out on a

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Table 1
Selected ^{1}H NMR data of compound **2**–**8**

H	2	3	4	5	6	7	8
3	3.77	3.29	3.77	3.76	3.76	3.76	3.77
6	5.41	5.37	5.37	5.37	5.38	5.37	5.37
4	2.52	2.25	2.54	2.53	2.53	2.54	2.54
18	0.89	0.89	0.67	0.63	0.92	0.79	0.80
19	1.06	1.03	1.03	1.03	1.03	1.05	1.06
16					6.71	4.41	
17						1.78	

MOD 1106 analyzer. Infrared spectra were recorded on a Thermo Nicolet 200 spectrometer using KBr disks in the 400–4000 cm^{-1} region. Melting-points were measured on a WC-1 melting-point apparatus and are uncorrected. Survey spectra (including ^{1}H NMR, ^{13}C NMR, homonuclear correlation (COSY), heteronuclear single quantum coherence spectra (HSQC), heteronuclear multiple-bond correlation spectra (HMBC), and DEPT) were obtained on a Bruker DPX-400 instrument with Me_4Si as the internal standard. Chemical shifts are given in δ values. Selected ^{1}H and ^{13}C NMR spectral data are reported in Table 1 and 2. High-resolution mass spectra were recorded with a Q-TOF micro mass spectrometer.

X-ray crystal analysis was made on a Rigaku RAXIS-IV imaging plate with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were refined isotropically. All calculations were performed using the SHELX-97 crystallographic software package [19].

Table 2
Selected ^{13}C NMR data of compound **2**–**8**

C	2	3	4	5	6	7	8
1	39.0	39.9	39.1	38.7	34.6	39.0	39.1
2	33.3	29.7	33.4	33.3	33.3	33.3	33.3
3	60.0	76.2	60.4	60.1	60.1	60.2	60.1
4	43.3	37.3	43.4	43.3	43.4	43.3	43.3
5	141.1	141.5	140.8	140.8	141.4	140.8	140.9
6	121.7	120.6	122.5	122.2	121.8	122.2	122.1
7	31.4	31.4	31.9	31.7	31.5	31.9	31.6
8	31.4	31.4	31.8	31.7	30.1	31.3	31.4
9	50.2	50.3	50.1	49.9	50.4	49.9	50.0
10	36.5	36.9	36.4	36.4	36.6	36.5	36.4
11	20.3	20.3	21.0	20.9	20.5	20.7	20.4
12	30.7	30.8	39.7	39.1	39.0	39.7	36.7
13	47.5	47.5	42.3	43.9	46.1	40.2	42.3
14	51.7	51.7	56.7	56.8	56.4	56.4	51.0
15	21.9	21.9	24.3	24.4	32.2	31.8	23.5
16	35.8	35.8	28.2	22.8	144.3	80.8	27.5
17	220.9	221.3	56.2	63.7	155.3	62.0	82.7
18	13.5	13.5	11.9	13.2	15.7	16.3	11.9
19	19.3	19.4	19.3	19.2	19.2	19.3	19.3
20			35.8	209.4	196.8	41.6	
21			18.7	31.5	27.1	14.5	

*2.2. 3β-Chloro-androst-5-en-17-one (**2**) and bis-(3β-androst-5-en-17-one) ether (**3**)*

Anhydrous $FeCl_3$ (85 mg, 0.52 mmol) was added at room temperature into a stirring solution of DHEA (**1**, 150 mg, 0.52 mmol) in dry CH_2Cl_2 (5 mL). After the disappearance of **1** as detected by TLC monitoring (5 h) by using 10:1 petrol ether–EtOAc, H_2O (2 mL) was added to the mixture. The organic layer was separated and dried over anhydrous Na_2SO_4, followed by fractionation by chromatography with 15:1 petrol ether–EtOAc, to afford **2** (115 mg, 72% yield), along with a 13% yield of by-product **3**.

*2.2.1. 3β-Chloro-androst-5-en-17-one (**2**)*

mp 151–152 °C, $[\alpha]_D^{20}$ +10.0° (*c* 0.28, $CHCl_3$). IR (KBr): 2947, 2860, 1734 cm^{-1}. HRMS: Calcd. for $C_{19}H_{27}ClO$: *m*/*z* 306.1750 $[M]^+$. Found: *m*/*z* 329.1648 $[M + Na]^+$, 331.1618 $[M + 2 + Na]^+$. *Anal*. Calcd. for $C_{19}H_{27}ClO$: C, 74.36; H, 8.87. Found: C, 74.67; H, 8.82.

Crystal data: $C_{19}H_{27}ClO$, $M = 306.86$, Monoclinic, $a = 6.5364(13)$, $b = 7.6371(15)$, $c = 17.067(3)$ Å, $\alpha = 90°$, $\beta = 96.77(3)°$, $\gamma = 90°$, $V = 846.0(3)$ $Å^3$, $T = 291(2)$ K, space group $P2(1)$, $Z = 2$, $D = 1.205$ Mg m^{-3}, μ(Mo Kα) = 0.224 mm^{-1}, θ range 1.20–27.48, $F(000) = 332$, 3061 reflection collected, 2938 unique [R(int) = 0.0236], final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0510$, $wR_2 = 0.1264$, R indices (all data): $R_1 = 0.0660$, $wR_2 = 0.1341$.

*2.2.2. Bis-(3β-androst-5-en-17-one) ether (**3**)*

mp 268–269 °C, $[\alpha]_D^{20}$ +16.0° (*c* 0.20, $CHCl_3$). IR (KBr): 2935, 2897, 2860, 1736, 1094 cm^{-1}. HRMS: Calcd. for $C_{38}H_{54}O_3$: *m*/*z* 558.4073 $[M]^+$. Found: *m*/*z* 581.3965 $[M + Na]^+$. *Anal*. Calcd. for $C_{38}H_{54}O_3$: C, 81.67; H, 9.74. Found: C, 81.88; H, 9.52.

*2.3. 3β-Chloro-5-cholestene (**4**)*

Using the same method as described above, 5-cholesten-3β-ol (cholesterol, 150 mg, 0.39 mmol) was treated with anhydrous $FeCl_3$ (63 mg, 0.39 mmol) to give **4** (109 mg, 69%): mp 90–91 °C, $[\alpha]_D^{20}$ −32.5° (*c* 0.35, $CHCl_3$). IR (KBr): 2940, 2861, 1464, 1378 cm^{-1}. HRMS: Calcd. for $C_{27}H_{45}Cl$: *m*/*z* 404.3210 $[M]^+$. Found: *m*/*z* 427.3112 $[M + Na]^+$, 429.3095 $[M + 2 + Na]^+$. *Anal*. Calcd. for $C_{27}H_{45}Cl$: C, 80.05; H, 11.20. Found: C, 79.89; H, 11.36.

*2.4. 3β-Chloro-5-pregnen-20-one (**5**)*

Following the same procedure as in Section 2.2, 3β-hydroxy-5-pregnen-20-one (120 mg, 0.38 mmol) was treated with anhydrous $FeCl_3$ (62 mg, 0.38 mmol) to furnish **5** (93 mg, 73%): mp 85–86 °C, $[\alpha]_D^{20}$ +33.5° (*c* 0.46, $CHCl_3$). IR (KBr): 2923, 2853, 1745, 1232, 1039 cm^{-1}. HRMS: Calcd. for $C_{21}H_{31}ClO$: *m*/*z* 334.2063 $[M]^+$. Found: *m*/*z* 357.1955 $[M + Na]^+$, 359.1946 $[M + 2 + Na]^+$. *Anal*. Calcd. for $C_{21}H_{31}ClO$: C, 75.31; H, 9.33. Found: C, 75.11; H, 9.45.

2.5. 3β-Chloro-5,16-pregnadien-20-one (6)

Following the same procedure as Section 2.2, 3β-hydroxy-5,16-pregnadien-20-one (120 mg, 0.38 mmol) was treated with anhydrous $FeCl_3$ (62 mg, 0.38 mmol) to give **6** (91 mg, 72%): mp 145–146 °C, $[\alpha]_D^{20}$ −22.1° (*c* 0.24, $CHCl_3$). IR (KBr): 2934, 2863, 1660, 1589, 1372 cm^{-1}. HRMS: Calcd. for $C_{21}H_{29}ClO$: *m/z* 332.1907 $[M]^+$. Found: *m/z* 355.1801 $[M + Na]^+$, 357.1780 $[M + 2 + Na]^+$. *Anal*. Calcd. for $C_{21}H_{29}ClO$: C, 75.76; H, 8.78. Found: C, 75.67; H, 8.85.

2.6. (25R)-3β-chlorospirost-5-ene (7)

Following the same procedure as in Section 2.2, (25*R*)-spirost-5-en-3β-ol (diosgenin, 130 mg, 0.30 mmol) was treated with anhydrous $FeCl_3$ (49 mg, 0.30 mmol) to afford **7** (90 mg, 69%): mp 175–176 °C, $[\alpha]_D^{20}$ −116.3° (*c* 0.22, $CHCl_3$). IR (KBr): 2946, 2907, 2868, 1455, 1051 cm^{-1}. HRMS: Calcd. for $C_{27}H_{41}ClO_2$: *m/z* 432.2795 $[M]^+$. Found: *m/z* 433.2870 $[M + H]^+$, 435.2847 $[M + 2 + H]^+$. *Anal*. Calcd. for $C_{27}H_{41}ClO_2$: C, 74.88; H, 9.54. Found: C, 74.77; H, 9.56.

2.7. 3β,17β-3-Chloro-androst-5-ene-17-acetate (8)

Following the same procedure as in Section 2.2, 3β,17β-androst-5-ene-3,17-diacetate (120 mg, 0.32 mmol) was treated with anhydrous $FeCl_3$ (52 mg, 0.32 mmol) to afford **8** (76 mg, 68%): mp 180–181 °C, $[\alpha]_D^{20}$ −50.8° (*c* 0.24, $CHCl_3$). IR (KBr): 2943, 2852, 1731, 1264, 1040 cm^{-1}. HRMS: Calcd. for $C_{21}H_{31}ClO_2$: *m/z* 350.2013 $[M]^+$. Found: *m/z* 373.1911 $[M + Na]^+$, 375.1893 $[M + 2 + Na]^+$. *Anal*. Calcd. for $C_{21}H_{31}ClO_2$: C, 71.87; H, 8.90. Found: C, 71.68; H, 9.05.

3. Results and discussion

The treatment of the solution of DHEA (**1**) in methylene chloride with an equivalent amount of anhydrous ferric chloride at room temperature afforded the main product (**2**) with a 72% yield, along with a 13% yield of the by-product **3**. The two products displayed lower polarity than DHEA. In the ^{13}C NMR spectrum of **2**, the C-3 signal appeared at δ60.0, an upfield shift of 11.6 ppm from δ71.6 in DHEA. The corresponding H signal downshifted to δ3.77 from δ3.54. In the HRMS spectrum of **2**, the $M + Na^+$ peak at *m/z* 329.1648 and the $M + 2 + Na^+$ peak at *m/z* 331.1618, as well as the 3:1 ratio of the heights of the two peaks, indicated that the formula of **2** was $C_{19}H_{27}ClO$. Thus, we concluded that **2** is the chlorine-exchanging product, 3-chloro-androst-5-en-17-one. The absolute configuration of C-3 could not be determined straightforwardly from the ^1H NMR spectra due to the presence of complicated multi-coupling. Fortunately, an X-ray crystal analysis of a suitable crystal of **2** confirmed that the chloro group at C-3 had an equatorial orientation as shown in Fig. 1, identical to that of the 3-OH in DHEA. Thus, the chlorine-exchanging reaction furnished a product that retained its configuration.

We concluded that the by-product **3** was bis-(3β-androst-5-en-17-one) ether based on the following facts: the ^{13}C NMR spectrum for **3** gave 19 carbon signals, including one carbon linked to oxygen (C-3), one carbonyl group, two double-bond carbons, and two CH_3; the NMR shift values of H-3 and C-3 were 3.29 and 76.2, respectively; the compound could not be acetylated with acetic anhydride and pyridine; the HRMS spectrum gave $M + Na^+$ peak at *m/z* 581.3965; and finally, the elemental analysis supported the assignment. The reaction is outlined in Scheme 1.

In order to further investigate the features of the reaction, DHEA was reacted with $FeCl_3$ under different conditions. The reaction conditions and results are summarized in Table 3. From entries 1–4, we noted that with an increase in the amount of $FeCl_3$ used in the reaction, the yield of **2** gradually became higher as the yield of **3** became lower. After the mol ratio reached 1:1, the yield of **2** did not increase further despite an increase in $FeCl_3$. When various solvents were used in the reaction, we found that the solvents with low polarity (entries 1–5) were favorable to the reaction, and that no reaction took place in the solvents with higher polarity or in protonic solvents (entries 7–10).

The generality and the scope of the chlorine-exchanging reaction was investigated by using some other steroids as

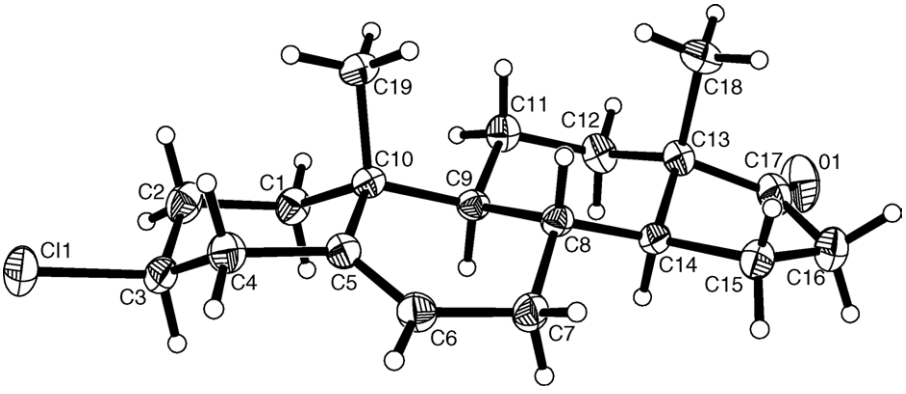
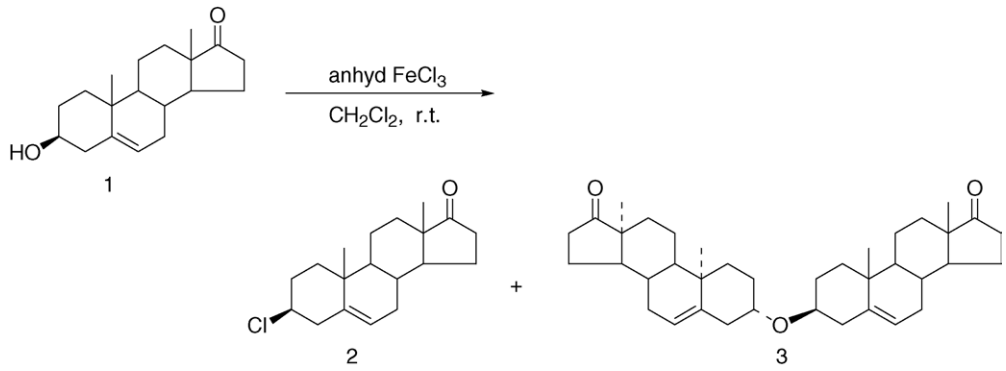


Fig. 1. ORTEP diagram of compound **2**.



Scheme 1. Treatment of DHEA with anhydrous $FeCl_3$.

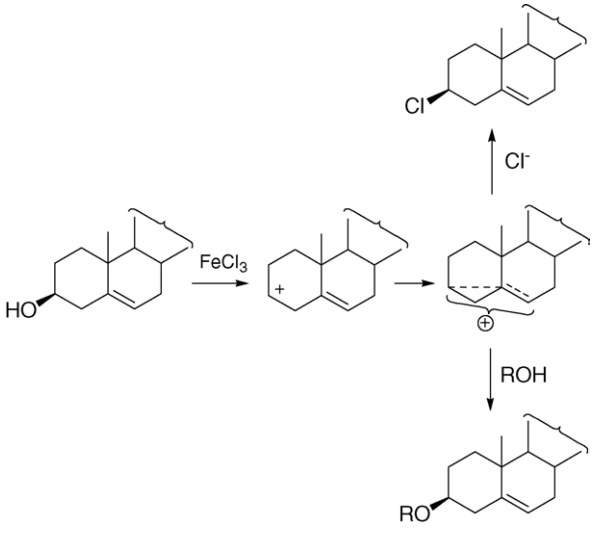
Table 3
Summary of the reaction conditions and results

Entry	$FeCl_3$:DHEA (mol ratio)	Solvent	Time (h)	Product, yields (%)		Total yields (%)
1	0.5:1	CH_2Cl_2	48	**2**, 56	**3**, 25	81
2	0.7:1	CH_2Cl_2	24	**2**, 65	**3**, 18	83
3	1.0:1	CH_2Cl_2	5	**2**, 72	**3**, 13	85
4	1.2:1	CH_2Cl_2	5	**2**, 71	**3**, 12	83
5	1:1	$CHCl_3$	5	**2**, 71	**3**, 13	84
6	1:1	EtOAc	24	**2**, 24	**3**, 6	30
7	1:1	THF	24	–		–
8	1:1	MeCN	24	–		–
9	1:1	DMF	24	–		–
10	1:1	EtOH	24	–		–

starting substrates. The results are detailed in Table 4. Among the attempted samples, all of the reactions of the 3β-hydroxyl-5-Δ steroids containing only one hydroxyl group (entries 2, 11–14) carried out well and afforded corresponding transformation-products in reasonable yields. But with the 3β,17β-androst-5-ene-3,17-diol, the reaction went forward with difficulty due to poor solubility in CH_2Cl_2. When it was first converted into 3,17-diacetate and then treated with anhydrous $FeCl_3$, the product with conversion in the 3-position but retention in the 17-position was formed (entry 15). And when steroids without the 5,6-olefinic group in their structure (entries 17–18) were used, no transformation took place at all. This result reveals that the 5,6-olefinic group plays a crucial role in the transformation.

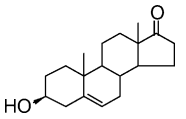
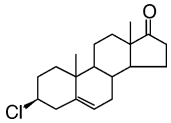
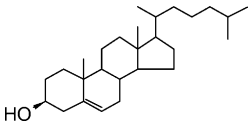
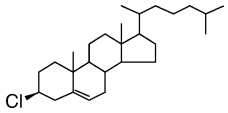
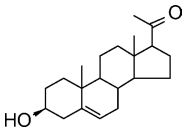
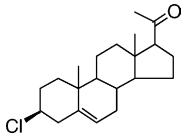
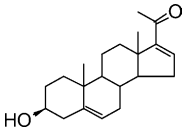
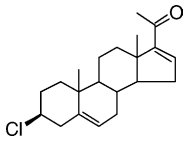
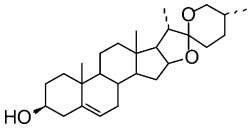
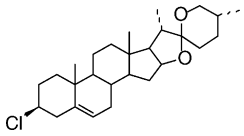
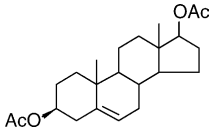
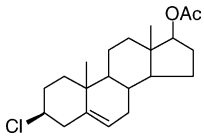
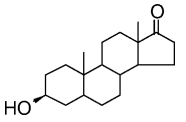
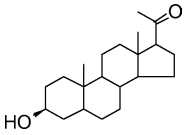
According to the results described above, we speculate that the reaction must have gone through a S_N1 mechanism involving the participation of the homoallylic carbonium ion [14], similar to that observed with other chlorination reagents [13]. Under the action of the Lewis acid $FeCl_3$, the 3β-hydroxyl-5-Δ steroid lost a hydroxyl group to form a non-classical carbonium ion intermediate, in which 5,6-olefinic group interacted with the carbonium ion at C-3 to form the homoallylic ion with partial 3,5-bonding and weakened 5,6-bonding. This intermediate reacted with nucleophiles Cl^- and ROH to furnish the chloride **2** and the ether **3**, respectively. The pathway is outlined in Scheme 2. The saturated steroids could not be chlorinated because they are unable to form the resonant homoallylic ion. The solvents with high polarity and the protonic solvents, perhaps significantly increasing the ionization of $FeCl_3$ and thereby reducing its action, were unfavorable to the reaction.

In conclusion, we describe the first use of $FeCl_3$ as a chlorination reagent in the chlorination of 3-hydroxy-5-Δ steroids under mild conditions, in a simple process, and with a reasonable yield. The reaction affords the alkyl chlorides with a retention of configurations. The 5,6-olefinic group in the



Scheme 2. Proposed pathway of the chlorine-exchanging reaction.

Table 4
The reaction of various steroids with $FeCl_3$[a]

Entry	Steroid	Product	Isolated yield (%)[b]
2			72
11			69
12			73
13			72
14			69
15			68
16		–	
17		–	

[a] Reaction conditions: room temperature; reaction time: 5 h; $FeCl_3$:steroid = 1:1.
[b] By-product ethers except for **3** were not collected.

starting material and a low-polarity solvent are necessary for the transformation.

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Appendix A. Supplementary Data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-259348. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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